KFM 33: Focus Session: (Multi-)Ferroic States V

The focus session is dedicated to (multi)ferroic states at interfaces and in heterostructures. The design of (emergent) properties at interfaces, modelling methods and advanced characterization tools will be of interest. Typical examples may include electrostatic and strain boundary conditions at interfaces, domains and domain walls in (multi)ferroics and applications in nano-electronic device.

Chair: Nives Strakalj (Institute of Physics, Zagreb)

Time: Friday 9:30–12:25 Location: EMH 225

KFM 33.1 Fri 9:30 EMH 225

Landau free energy of $PbTiO_3$ from atomistic simulations — •Mauro Pulzone[1,2], Natalya S. Fedorova[1], Hugo Aramberri[1], and Jorge Íñiguez-González[1,2] — [1]Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg — [2]University of Luxembourg, Esch-sur-Alzette, Luxembourg

In this study we introduce a methodology to identify and compute, from atomistic simulations, the simplest Landau potential that accurately describes the static properties of $PbTiO_3$ as a function of temperature. The free energy of the system is expanded around the reference cubic phase in powers of the polarization. We consider all possible combinations of symmetry-allowed terms from 2^{nd} up to 10^{th} order. We fit all these models using the approach of Ref. [Phys. Rev. B 63, 144103 (2001)], taking as input the data obtained from Monte Carlo simulations based on the atomistic second-principles model for $PbTiO_3$ proposed by Wojdeł et al. [Phys.: Condens. Matter 25, 305401 (2013)].

We find that a 6^{th}-order expansion is sufficient to capture the system's behavior, including the first-order character of the transition. Moreover, as the temperature increases (hundreds of Kelvins above the phase transition) a 4^{th}-order model is enough to reproduce the atomistic data accurately.

Presently we are extending this work to explicitly consider the strain as an order parameter, as the elastic deformation of the cell is known to play an essential role in the first-order character of the phase transition of $PbTiO_3$ [Phys. Rev. B 55, 6161 (1997)].

KFM 33.2 Fri 9:50 EMH 225

Reversible thermal conductivity switching in barium titanate ceramics — •Lucile Féger, Nassima Radouane, Fabien Giovannelli, Julien Bustillo, Nathalie Poirot, Guillaume F. Nataf, and Isabelle Monot-Laffez — GREMAN UMR7347, CNRS, University of Tours, INSA Centre Val de Loire, 37000 Tours, France

Control of charge flows led to the invention of the transistor and all related electronic devices of our daily life. In contrast, manipulating heat flows is still a challenge and this trend is driven by the constant pursuit of novel properties, efficiency, and functionality in technological applications. Yet, heat management is essential in electronic circuits and may lead to the development of a new paradigm of logic (phononics) [1]. Ferroelectric materials are a promising class of materials to design thermal switches, due to the strong dependence of their properties to an applied electric field. Here we investigate the evolution under an electric field of the thermal conductivity of barium titanate. For this purpose, we adapted a laser flash system to be able to apply a voltage in-situ. We then measured at different temperatures the thermal conductivity of ceramics of barium titanate with different grain sizes: 0.5, 5, 50 and 100 micrometers. We show reversible changes in thermal conductivity under the application of an electric field in-situ, which are compared to measurements where the electric field is applied ex-situ [2]. We discuss our results based on changes in polarization and domain structures induced by the electric field. [1] Li, N. et al. Reviews of Modern Physics, 84 (2012). [2] Lin, Y. et al. ACS Applied Materials & Interfaces,14 (2022).

KFM 33.3 Fri 10:10 EMH 225

An extended phase-field-drift-diffusion model for oxygen vacancy migration in single-crystal barium titanate — •Xuejian Wang and Frank Wendler — Institute of Materials Simulation (WW8), Friedrich-Alexander-Universität Erlangen-Nürnberg, Dr.-Mack-Str. 77, 90762 Fürth, Germany

Barium titanate (BTO) and its solid solutions are attractive materials for replacing lead-based piezoelectrics, exhibiting a high density of point defects. Here, we present an extended phase-field model that includes the migration of oxygen vacancies (Vo), a crucial type of point defect in ferroelectric materials, within single-crystal BTO. The model bases on the Landau-Ginzburg-Devonshire theory, considers a continuous concentration of Vo (Cv) and incorporates the drift-diffusion equation for its migration. The Finite Element Method is used to simulate domain formation with varying Cv values, where a range of phenomena is discovered. Initially, the existence of Vo induces a modification in the orientation of polarization in comparison to the defect-free crystal. The level of Cv significantly affects the evolution and structure of domain/domain walls (DWs). Systems possessing a larger Cv will generate domains of higher density and a greater variety of DWs in comparison to systems with lesser Cv. The migration of Vo occurs on both sides of the DWs and along the polarization orientation. Moreover, defect clustering is observed at the junctions of domain walls at higher Cv levels. The influence of Vo concentrations on electromechanical loading are shown, and results are compared to experimental data from literature.

KFM 33.4 Fri 10:30 EMH 225

Parametrization of a ferroelectric phase-field model from MD including nucleation data — •Frank Wendler[1], Dilshod Durdiev[1], Michael Zaiser[1], Takahiro Tsuzuki[2], Hikaru Azuma[2], Shuji Ogata[2], Ryo Kobayashi[2], and Masayuki Uranagase[2] — [1]Institute of Materials Simulation, Friedrich-Alexander-Universität Erlangen-Nürnberg, Dr.-Mack-Str. 77, 90762 Fürth, Germany. — [2]Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-9555, Japan

Phase-field models based on the Landau-Ginzburg-Devonshire theory extend the time and length scales in comparison to molecular dynamics (MD) simulations, and enable a bottom-up approach to generate a complete energy landscape purely from atomistic information.Crucial material parameters such as elastic and piezoelectric properties, kinetic coefficients, as well as domain wall characteristics are extracted from MD data to adjust anisotropic gradient energy. To bridge the gap between the atomistic and continuum model, a proposed parametrization workflow involves determining all coefficients for the 6th order Landau polynomial from polarization reversal characteristics. Polarization switching in ferroelectric barium titanate (BTO) involves localized nucleation and subsequent domain growth, driven by an applied electric field. MD simulation data proves the role of thermal activation in domain nucleation, resulting in a notable scatter in coercive fields within small systems. From this data we calculate the activation parameters for BTO that govern polarization switching at coercive fields not only for perfect, but also those containing vacancy defects.

15 min. break

KFM 33.5 Fri 11:05 EMH 225

Field dependence of the electrocaloric effect in ferroelectrics with first order and diffuse phase transitions — •Jan Fischer, Daniel Haegele, and Joerg Rudolph — Ruhr University Bochum

The electrocaloric effect (ECE) in ferroelectrics is currently in the focus of interest for energy efficient cooling technologies. The field dependence $\Delta T_{\mathrm{ad}}(E)$ of the adiabatic caloric temperature change as a key parameter of caloric materials is highly relevant both for the fundamental understanding of the ECE and for the design of caloric coolers. Traditionally, $\Delta T(E)$ has been measured only for discrete values of the electric field and the low-field range is often left unexplored.

Here, we present high-resolution measurements of the electric field dependence $\Delta T(E)$ by dynamic measurements of the IR radiation emitted by the sample [1]. We find characteristic changes of $\Delta T(E)$ within a few Kelvin as a fingerprint of the first order phase transition in $BaTiO_3$. In contrast, investigations of $Ba(Zr_{0.12}Ti_{0.88})O_3$ show only a slow and gradual change of the field dependence over a broad temperature range as a consequence of the diffuse phase transition. Simultaneous measurements of the polarization P further allow to compare the polarization dependence $\Delta T(P)$ to predictions of Landau-Devonshire theory. In addition, single-shot measurements of the dynamics $\Delta T(t)$

for few-cycle bursts of the electric field allow, e.g., to separate hysteresis heating from the pure caloric temperature change.
[1] Fischer *et al.*, Rev. Sci. Instrum. 94, 043906 (2023)

KFM 33.6 Fri 11:25 EMH 225

Towards precise domain-wall engineering in $BaTiO_3$-based materials — •Sheng-Han Teng[1], Aris Dimou[1], Chinwendu Nancy Anabaraonye[2,3], and Anna Grünebohm[1] — [1]Interdisciplinary Centre for Advanced Materials Simulation (ICAMS) and Center for Interface-Dominated High Performance Materials (ZGH), Ruhr-University Bochum, Germany — [2]Institute for Physical Chemistry, University of Münster, Corrensstraße 28/30, 48149 Münster, Germany — [3]International Graduate School for Battery Chemistry, Characterization, Analysis, Recycling and Application (BACCARA), University of Münster, Corrensstraße 40, 48149 Münster, Germany

Domain walls in ferroelectric oxides are promising for new nanoelectronic device concepts [1]. However, precise control of domain walls and their dynamics remains a challenge [2]. In the present work, we use *ab initio* based effective Hamiltonian [3] to explore how local point defects and nanoscale inclusions can affect phase and domain structure as well as wall pinning, bowing, and roughness in BaTiO3-based materials.

[1] D. Meier, S. M. Selbach, *Nat. Rev. Mater.* **7**(3), pp. 157–173 (2022)

[2] A. Grünebohm, M. Marathe, R. Khachaturyan, R. Schiedung, D. C. Lupascu, V. V. Shvartsman, *J. Phys. : Condens. Matter.* **34**(7), p. 073002 (2021)

[3] W. Zhong, D. Vanderbilt, K. M. Rabe, *Phys. Rev. B* **52**(9), pp. 6301–6312 (1995)

KFM 33.7 Fri 11:45 EMH 225

Direct probing of dislocation-controlled domain nucleation and domain-wall pinning in single-crystal BaTiO3 by multi-stimuli MEMS-based in situ TEM — •Tianshu Jiang[1], Fangping Zhuo[1], Oscar Recalde-Benitez[1], Yevheniy Pivak[2], and Leopoldo Molina-Luna[1] — [1]Institute of Materials Science, Department of Materials and Earth Sciences, Technical University of Darmstadt, Darmstadt, Germany — [2]DENSsolutions, Informaticalaan 12, Delft, The Netherlands

Engineering domain walls to control their nanoscale mobility influences macroscopic properties, crucial for electromechanics and electronics. This is evident in imprinting topological defects in materials, highlighting the field's potential. However, despite the critical role of defect-mediated domain nucleation and domain wall mobility, our comprehensive understanding of these phenomena remains limited. Here, we explore the dislocation-mediated domain nucleation and domain wall mobility in single-crystal BaTiO3 at nanoscale by applying multi-stimuli MEMS-based in situ transmission electron microscopy (TEM). A dense, well-aligned "forest" of dislocations, intentionally imprinted, serves to selectively nucleate in-plane domain variants. Utilizing multi-stimuli in situ TEM, we highlight the direct observation of the pinning of ferroelastic domain walls by these imprinted dislocations. This strong pinning of domain walls results from the stress fields associated with the imprinted dislocations. Our findings advance domain wall engineering in ferroelectrics, offering a novel strategy for advanced nanoelectronics and bulk applications over a broad temperature range.

KFM 33.8 Fri 12:05 EMH 225

Intrinsic strain engineering by dislocation imprint in single-crystal BaTiO3 — •Fangping Zhuo and Jürgen Rödel — Department of Materials and Earth Sciences, Technical University of Darmstadt, 64287 Darmstadt, Germany

Dislocations exert significant control over strain, and charge in ferroelectrics, extending beyond the constraints of traditional bulk doping. In these materials, they not only act as nucleation sites for domain formation and pinning centers for the motion of domain walls, but also offer underappreciated potential in bulk ferroelectrics.

Our focus will be on a novel approach to manipulate the mobility of ferroelectric domain walls and piezoelectricity of single-crystal BaTiO3. By employing controlled high-temperature plastic deformation along the [110] direction, we have effectively enhanced the dielectric and piezoelectric coefficient. This was achieved by harnessing the anisotropic interactions between 1D dislocations and 2D domain walls. We will delve into means of minimizing domain instability and extrinsic degradation processes through strategic strain adjustment, balancing in-plane and out-of-plane domain variants. Direct observation of domain-wall pinning of 90° domain walls by dislocations was documented using in situ transmission electron microscopy. We will highlight the innovative application of intrinsic strain engineering in bulk ferroelectrics, demonstrating plastic deformation as a key technique to customize microstructures and functionalities in these materials.